

PATENT SPECIFICATION

945,580

NO DRAWINGS.

945,580



Date of Application and filing Complete Specification :
Feb. 13, 1962.
No. 5506/62.

Application made in United States of America (No. 94142)
on March 8, 1961.

Complete Specification Published : Jan. 2, 1964.

© Crown Copyright 1964.

Index at Acceptance :—Class C3 T6B.

International Classification :—C 08 g.

COMPLETE SPECIFICATION.

Improvements in or relating to Organosiloxanes.

We, Dow CORNING CORPORATION, of Midland, Michigan, United States of America, a Corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to organosiloxane compositions.

Because of their superior thermal stability and electrical properties organopolysiloxanes have long been used to insulate electrical and electronic equipment. When the insulation is in the form of relatively thin films any siloxane resin system can be satisfactorily employed. However, when the insulation is to be used in deep section many siloxane resins are unsuitable. One reason for this is the fact that many siloxane resin systems require a solvent carrier and/or evolve volatile constituents when they are cured. In both cases the removal of the volatile constituent (either solvent or reaction by-product) precludes cure in deep section since the formation of voids in the cured resin renders electrical properties of the resulting component unsatisfactory. This deficiency cannot be cured by vacuum impregnation since the voids are formed after the viscosity of the resin has reached a point where the volatile material can no longer escape.

35 There are other siloxane systems which can be cured without the formation of volatile constituents, but which require the presence of atmospheric moisture. Whereas, these systems do not form voids when cured in deep section, the cure thereof is extremely slow or incomplete due to the fact

that atmospheric moisture cannot penetrate into the middle of the resin mass.

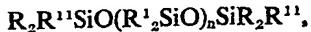
Another problem which has long plagued the siloxane encapsulation art has been the high coefficient of expansion exhibited by organosiloxanes. It is 10 to 15 times that of metals normally employed in electrical and electronic equipment. As a result, tremendous stresses are set up in the insulation when the encapsulated system is alternately heated and cooled. Consequently, heretofore employed siloxane encapsulating resins were often unsatisfactory because the thermal cycling caused cracking of the insulation. This cracking could of course be avoided by employing known siloxane elastomers.

However, unfilled siloxane elastomers at present known have an extremely low mechanical strength. For example, the tensile strength of an unfilled vulcanised dimethylpolysiloxane is in the order of 50 lbs./sq.in. Consequently, such materials do not have the mechanical strength required for many electrical applications. The mechanical strength of siloxane elastomers can be improved by employing fillers. However, such fillers render the mass either opaque or opalescent. Thus the elastomeric components cannot be seen through the insulating mass.

This is a matter of great importance since in many electric systems the individual components are quite inexpensive, whereas the finished system may be worth a great deal of money. However, when the material has been encapsulated in an opaque insulating material and one of the cheap components fails, there is no way of determining which one has failed. Consequently the entire system is often discarded.

It is the object of this invention to provide a transparent encapsulated material which has the required mechanical strength and flexibility to give satisfactory service over a wide range of temperature conditions and under severe mechanical stresses. Another object is to provide a material through which the individual components of an electric system can be seen and which will allow replacement of such components without running the insulation of the entire system.

This invention provides a composition consisting essentially of (1) an essentially linear polysiloxane of the general formula

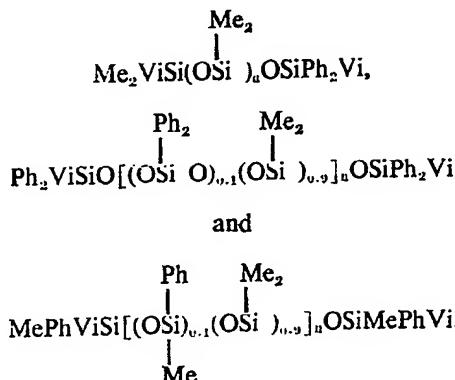


if desired containing up to 1 mol % of $SiO_{1.5}$ units in which each R and each R^1 is a monovalent hydrocarbon radical free from aliphatic unsaturation and at least 85 mol per cent of the R^1 groups are methyl radicals, and R^{11} is an alkenyl radical, preferably a vinyl radical, said siloxane (1) having a viscosity of from 500 to 10,000 cs. inclusive at 25° C., (2) from 20 to 50 per cent by weight calculated on the weight of (1) and (2) of a co-polymer of SiO_2 , $(CH_3)_3SiO_{0.5}$ and $(CH_3)_2R^{11}SiO_{0.5}$ siloxane units in which co-polymer there is from 1.5 to 3.5 per cent by weight of alkenyl, preferably vinyl, radicals calculated on the weight of (2) and in which co-polymer (2) the ratio of total $(CH_3)_3SiO_{0.5}$ and $(CH_3)_2CH_2=CHSiO_{0.5}$ to SiO_2 units is from 0.6:1 to 1:1, (3) a compound compatible with (1) and (2) which is a siloxane containing from 0.4 to 1.4 per cent by weight of silicon-bonded hydrogen atoms, the remaining valencies of the silicon atoms in (3) being satisfied by monovalent hydrocarbon radicals free from aliphatic unsaturation, there being at least three silicon-bonded hydrogen atoms per molecule, and in (3) any hydrocarbon radicals attached to a silicon having hydrogen bonded thereto being essentially all methyl radicals, the amount of (3) being such that there is from 0.75 mol of SiH per mol of alkenyl, preferably vinyl, radicals in (1) and (2) to 1.5 mol of SiH per mol of alkenyl, preferably vinyl, radicals in (1) and (2), and (4) a platinum catalyst.

The composition of this invention is best cured by heating at a temperature of from 100° to 200° C., whereupon curing proceeds in one hour or less. It is believed that this curing is brought about by the reaction of the SiH containing component (3) to the alkenyl radicals, preferably vinyl radicals, in (1) and (2). Preferably the mixture should be used within a few hours after mixing the four ingredients, although the shelf life can be extended for days by cooling to temperatures of -20° C. or below.

The compositions of this invention are liquid materials which are readily pourable and can be used to impregnate complicated equipment. They can also be used to form cast articles of any desired shape.

For the purpose of this invention component (1) is a co-polymer of two or more siloxane units. Specific examples of such co-polymers are

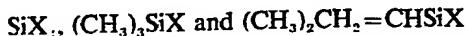


In all of the above examples n is of sufficient value to produce a viscosity of 500 to 10,000 cs. at 25° C., Me is methyl, Vi is vinyl and Ph is phenyl. The phenyl radicals can be replaced by any alkyl, cycloalkyl, aralkyl, alkaryl or other aryl radical in the foregoing formulae.

For the purpose of this invention it is essential that component (2) be employed in amount from 20 to 50 per cent by weight of the combined weights of (1) and (2). Compound (2) is a co-polymer of the three specified siloxane units. It is essential that the weight per cent of the alkenyl radicals, preferably vinyl radicals in said co-polymers be from 1.5 to 3.5 per cent calculated on the weight of (2). These per cents are calculated on the weight of the alkenyl, preferably vinyl radical, that is 27. In order to obtain transparent materials it is essential that the total trimethylsiloxane units and dimethylalkenylsiloxane units relative to the SiO_2 units in (2) shall range from 0.6:1 to 1:1.

Co-polymers (1) can be prepared by any of the conventional methods for preparing triorganosilyl end-blocked diorganosilylpolysiloxanes. This can be done, for example, by co-hydrolysing the corresponding chloro- or alkoxy silanes, or by equilibrating the corresponding hexaorganodioorganosiloxane with the corresponding diorganosiloxane in the presence of an alkaline or acid catalyst.

Co-polymers (2) can be prepared by the co-hydrolysis of the silanes of the general formulae

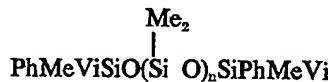


- in the proper proportions to give the desired ratios. X is halogen or alkoxy radical. Alternatively the co-polymer can be prepared by the procedure described in Specification No. 706,719. This involves reacting a silica hydrosol with hexamethyl-disiloxane or trimethylchlorosilane and with dimethylvinylchlorosilane or trimethylchlorosilane and with dimethylvinylchlorosilane or divinyldisiloxane. The latter can be reacted with the silica hydrosol either simultaneously with or subsequently to reaction with the trimethylchlorosilane or hexamethyldisiloxane. Preferably the vinyl constituent is reacted with the hydrosol subsequently to the trimethylsilyl constituent.
- Another critical component of the composition of this invention is co-polymer (3) which must be employed in amount sufficient that the ratio of mols of silicon-bonded hydrogen in the overall composition relative to the mols of silicon-bonded alkenyl, preferably vinyl, radicals in (1) and (2) shall be within the range 0.75:1 to 1.5:1. Compound (3) must be compatible with (1) and (2) if a transparent material is to be obtained. Furthermore, in order to obtain an operative material the per cent by weight of silicon-bonded hydrogen in (3) must be within the range of 0.4 to 1.4 inclusive per cent by weight calculated on the weight of (3). In order for (3) to serve as a cross-linker for the systems, there must be at least three silicon-bonded hydrogens per molecule.
- Furthermore, in the case of those silicon atoms in (3) which have both hydrogen and hydrocarbon radicals bonded thereto, essentially all these hydrocarbon radicals should be methyl. The term "essentially all" means that the presence of some PhHSiO groups is not precluded. However, if such groups are present there must also be at least three MeHSiO, Me₂HSiO_{1/2} or HSiO_{3/2} groups per molecule.
- Specific examples of (3) of which are within the scope of the invention are
- HSi(OSiMe₂H)₂)OSiMe₃,
- Me
|
Me₂Si(OSi)_nOSiMe₃ and Si(OSiMe₂H)₄
H
- co-polymers of SiO₂, Me₂SiO and Me₂HSiO_{1/2}; co-polymers of methyl hydrogen siloxane and phenylmethylsiloxane; co-polymers of methyl hydrogen siloxane, dimethylsiloxane and diphenylsiloxane and co-polymers of methyl hydrogen siloxane and dimethylsiloxane.
- Any finely divided form of platinum can be employed as the catalyst in this invention. This includes finely dispersed metallic platinum such as platinum dispersed on charcoal or other carriers, and soluble compounds of platinum such as chloroplatinic acid, or complexes of platinic chloride with olefins such as ethylene, propylene, butadiene and cyclohexane. Preferably the platinum should be in soluble form.
- The amount of platinum is not critical since it merely affects the rate of cure. However, for practical operation, it is preferred that the catalyst be employed in amount ranging from 0.5 to 20 parts per million calculated on the weight of (1), (2) and (3).
- After the four ingredients have been mixed in any desired manner, the composition is cured. The composition will cure very slowly at room temperature, but for most applications it is preferred that the mixture be heated at a temperature in the range 50° to 150° C. or above. This expedites the cure so that it will proceed in from less than one hour to several hours. Thus it can be seen that one can regulate the time of cure widely by regulating the temperature and the concentration of the platinum catalyst.
- If desired, fillers can be employed in the compositions of this invention. These fillers are used when optical clarity is not desired. The fillers operative in the present invention include any of the fillers normally employed in organopolysiloxanes such as fume silica, aluminium silicate, quartz, calcium carbonate, zirconium silicate, and metal oxides such as alumina, zinc oxide, titania and ferric oxide. If desired, the fillers can be treated with organosilicon compounds such as chlorosilanes or alkoxy silanes so as to produce a hydrophobic surface. The latter treatment is particularly desirable with finely divided silicas, such as fume silicas or silica aerogels.
- The compositions of this invention are useful for electrical insulation and for the formation of cast articles.
- The following examples illustrate the invention. The following abbreviations are employed herein, Me is methyl, Ph is phenyl and Vi is vinyl. In the following examples all parts and per cents are by weight and all viscosities were measured at 25° C. unless otherwise stated. In all copolymers (2) in the following examples the ratios of total Me₂SiO_{0.5} and Me₂ViSiO_{0.5} to SiO₂ units are in the range 0.6:1 to 1:1.

EXAMPLE 1.

115

65 per cent of (1) a 2,000 cs. viscosity siloxane of the formula



was mixed with (2) 35 per cent of a co-polymer of SiO_2 , $\text{Me}_3\text{SiO}_{1.5}$ and $\text{Me}_2\text{ViSiO}_{0.5}$ containing 2.5 per cent of vinyl radicals.

94.9 parts of the above mixture were
5 mixed with (3) 5.1 parts of $\text{PhSi(OSiMe}_2\text{H)}_3$
and 5 parts per million of platinum added
as chloroplatinic acid dissolved in 2-ethyl-
hexanol. The resulting mixture was cast
10 into a slab $8 \times 8 \times 1/16$ inches and cured for
one hour at 150°C . The resulting slab was
clear and had the following properties: —

Durometer			
(Shore scale) ...	54		
Tensile strength ...	750 lbs./sq.in.		
Elongation at break... 15	80 per cent		

The above mixture had a viscosity of 4500 cs. at 25°C . The material was cast around a steel hexagonal bar and cured for one hour at 150°C . It was then subjected
20 to thermal shock test Mil-I-16923 C in which the specimen was cycled from 155° to -55°C . ten times without cracking. This proves that the material has sufficient flexibility to withstand the stress caused by difference in
25 expansion between the siloxane and the metal inserts.

The above composition was also used to
pot an electronic printed circuit. The siloxane was cured for four hours at 65°C . to
30 give a clear mass through which each component of the circuit was visible. One of the components was replaced by cutting into the cured siloxane, replacing the component and then filling the hole with more uncured
35 siloxane. The filling material was then cured as above and the system performed in the same manner as it did prior to removal of the component. This shows the feasibility of replacing one component of an
40 insulated system without destroying the effectiveness of the insulation.

EXAMPLE 2.

A mixture of 55 per cent of composition (1) and 45 per cent of composition (2), both
45 of Example 1 was made. 94.9 parts of this

mixture were mixed with 5.1 parts of composition (3) of Example 1 and the catalyst of that example in an amount to give 3 parts per million of platinum. The resulting mixture had a viscosity of 18,000 cs. It was cast into a slab $8 \times 8 \times 1/16$ inches and then cured for one hour at 150°C . The resulting clear material had the following properties:

Durometer			
(Shore scale) ...	55		55
Tensile strength ...	840 lbs./sq.in.		
Elongation at break... 15	100 per cent		

EXAMPLE 3.

A liquid mixture was made containing 75 per cent of composition (1) of Example 1, and (2) 25 per cent of a co-polymer of SiO_2 , $\text{Me}_3\text{SiO}_{1.5}$ and $\text{Me}_2\text{ViSiO}_{1.5}$ units which co-polymer contained 2.7 per cent of vinyl groups.

100 parts of this mixture were mixed with 30 parts of diatomaceous earth, 5.1 parts of composition (3) of Example 1, and 3 ppm of platinum. The resulting material had a viscosity of 12,000 cs. The mixture was heated one hour at 150°C . and gave the following properties: —

Durometer			
(Shore scale) ...	54		
Tensile strength ...	770 lbs./sq.in.		
Elongation at break... 15	110 per cent		75

EXAMPLE 4.

This example shows the critical effect of the vinyl content of ingredient (2) of the claimed compositions.

In each case shown below the compositions employed were composed of 60 parts of ingredient (1) of Example 1, 40 parts by weight of each of the ingredients (2) shown in the table below, 2 ppm. platinum and a sufficient amount of ingredient (3) of Example 1 to give in each case a SiH to vinyl ratio of 1:1. Each formulation was cast into a slab of $8 \times 7 \times 1/16$ inches and then cured for one hour at 150°C .

TABLE I.

Run No.	% By Wt. Vi in Resin Ingred. (2)	Durrometer	Tensile lbs./sq.in.	% Elong. at break
1	3.5	61	590	70
2	2.95	56	790	80
3	2.70	50	930	110
4	1.70	35	600	190
5*	0.70	14	60	300

* For comparison only.

EXAMPLE 5.

Each of the samples shown in the table below was made by mixing 65 parts of ingredient (1) of Example 1 and 34 parts of ingredient (2) of Example 1. To these mixtures were added sufficient catalysts to give

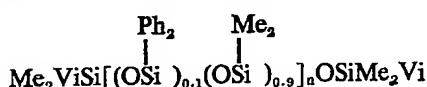
a 2 ppm. of platinum and sufficient of the ingredients (3) shown below to give in each case a SiH to vinyl ratio of 1.15:1. Each sample was cast into a slab $8 \times 8 \times \frac{1}{16}$ inches and then cured for one hour at 150° C. The properties were as shown below:—

TABLE II.

Ingredient (3)	Co-polymer Formulation	Per Cent by Wt. SH*	Durometer (Shore scale)	Tensile lbs./sq.in.	Per Cent Elongation at break
PhSiO _{3/2}	0.84	40	960	995	110
Me ₂ HSiO _{0.5}				580	100
HSiO _{3/2} SiO _{2/2}				1030	75
Me ₂ SiO and Me ₂ HSiO _{0.5}	1.08	49	46	105	
Me ₂ SiO _{n.5}	1.35	52			
MeHSiO					
Me ₂ HSiO _{0.5}					
MeHSiO	0.57				
Me ₂ SiO					

* Determined by analysis.

EXAMPLE 6.
A tough product was obtained when 65 parts of a 9,000 cs. liquid of the formula



- 5 were mixed with 35 parts of co-polymer (2) of Example 1 and 94.9 parts of this mixture were mixed with 4 parts of Si(OSiMe₂H)₂ and 20 ppm. of platinum in the form of platinum dispersed on charcoal, and the resulting mixture was heated for 12 hours at 10 50° C.

WHAT WE CLAIM IS:—

1. A composition consisting essentially of (1) an essentially linear polysiloxane of the general formula

15



if desired containing up to 1 mol % of RSiO_{1.5} units in which each R and each R¹ is a monovalent hydrocarbon radical free from aliphatic unsaturation, at least 85 mol per cent of the R¹ radicals being methyl and R¹¹ is an alkenyl radical in which siloxane (1) n has a value such that the viscosity of (1) is from 500 to 10,000 cs. inclusive at

20

- 25° C., (2) from 20 to 50 per cent by weight calculated on the total weight of (1) and (2) of a co-polymer of SiO_2 , $(\text{CH}_3)_3\text{SiO}_{0.5}$ and $(\text{CH}_3)_2\text{R}^{11}\text{SiO}_{0.5}$ siloxane units in which co-polymer there is from 1.5 to 3.5 inclusive per cent by weight of alkenyl radicals calculated on the weight of (2) and in which co-polymer (2) the ratio of the total $(\text{CH}_3)_3\text{SiO}_{0.5}$ and $(\text{CH}_3)_2\text{R}^{11}\text{SiO}_{0.5}$ units to SiO_2 units is from 0.6:1 to 1:1, (3) a compound compatible with (1) and (2) which is a siloxane containing from 0.4 to 1.4 per cent by weight of silicon-bonded hydrogen atoms, the remaining valencies of the silicon atoms in (3) being satisfied by phenyl and/or methyl radicals, there being at least three silicon-bonded hydrogen atoms per molecule and in (3) any hydrocarbon radicals attached to SiH silicon are essentially all methyl radicals, the amount of (3) being such that there is from 0.75 mols of SiH per mol of alkenyl radicals in (1) and (2) to 1.5 mol of SiH per mol of alkenyl radicals in (1) and (2), and (4) a platinum catalyst.
2. A composition as claimed in Claim 1 wherein the alkenyl radicals are vinyl radicals.
3. A process for the preparation of a cured siloxane composition which comprises mixing (1) a polysiloxane of the general formula



in which each R and R^1 is a monovalent hydrocarbon radical free from aliphatic unsaturation, at least 85 mol per cent of the R^1 radicals being methyl and R^{11} is an alkenyl radical in which siloxane (1) n has a value such that the viscosity of (1) is from 500 to 10,000 cs. inclusive at 25° C., (2)

from 20 to 50 per cent by weight calculated on the total weight of (1) and (2) of a co-polymer of SiO_2 , $(\text{CH}_3)_3\text{SiO}_{1/2}$ and $(\text{CH}_3)_2\text{R}^{11}\text{SiO}_{1/2}$ siloxane units in which co-polymer there is from 1.5 to 3.5 inclusive per cent by weight of alkenyl radicals calculated on the weight of (2) and in which co-polymer (2) the ratio of the total $(\text{CH}_3)_3\text{SiO}_{1/2}$ and $(\text{CH}_3)_2\text{R}^{11}\text{SiO}_{1/2}$ units to SiO_2 units is from 0.6:1 to 1:1, (3) a compound compatible with (1) and (2) which is a siloxane containing from 0.4 to 1.4 per cent by weight of silicon-bonded hydrogen atoms, the remaining valencies of the silicon atoms in (3) being satisfied by phenyl and/or methyl radicals, there being at least three silicon-bonded hydrogen atoms per molecule and in (3) any hydrocarbon radicals attached to SiH silicon being essentially all methyl radicals, the amount of (3) being such that there is from 0.75 mols of SiH per mol of alkenyl radicals in (1) and (2) to 1.5 mol of SiH per mol of alkenyl radicals in (1) and (2), and (4) a platinum catalyst, and thereafter curing the mixture.

4. A process as claimed in Claim 3 wherein the alkenyl radicals are vinyl radicals.

5. A process as claimed in Claim 3 substantially as described with reference to any one of the examples.

6. Cured siloxane compositions when prepared by the process claimed in any one of Claims 3 to 5.

ELKINGTON & FIFE,
Chartered Patent Agents,
Bank Chambers, 329 High Holborn,
London, W.C.1.
Agents for the Applicants.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.